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(56) Documents Cited
EP 0547546 A1 EP 0191736 A2 EP 0159290 A1
EP 0159287 A1 WO 97/45016 A1 US 5698539 A
US 5296449 A
Chemical Abstracts, abstr no 128:98850 & Brighton Crop Prot. Conf.--Weeds, 1997, Vol. 1, pages 39-44

(58) Field of Search
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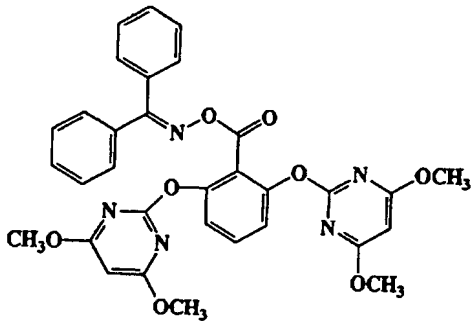
(54) Abstract Title
Antidotes for the herbicide pyribenzoxim [benzophenone O-{2,6-bis[(4,6-dimethoxy-2-pyrimidyl) oxy]benzoyl}oxime], especially cloquintocet & fenchlorazole

(57) A method of reducing phytotoxicity to crop plants caused by the herbicide pyribenzoxim, which is benzophenone O-{2,6-bis[(4,6-dimethoxypyrimidyl)oxy]benzoyl}oxime and has the formula (I), comprises applying to the locus of the crop plant, the crop or crop plant seed an antidotally effective amount of an antidote effective to pyribenzoxim.



(I)

As an antidote are included 5-chloroquinoline-8-yloxy acetic acid; or a salt or ester thereof (especially the 1-methylhexyl ester thereof, ie cloquintocet-mexyl) and 1-(2,4-dichlorophenyl)-5-trichloromethyl)-1H-1,2,4-triazole-3-carboxylic acid, or a salt or ester thereof (especially the ethyl ester thereof, ie fenchlorazole-ethyl).

Compositions of such antidotes and pyribenzoxim are disclosed.

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New Herbicidal Compositions

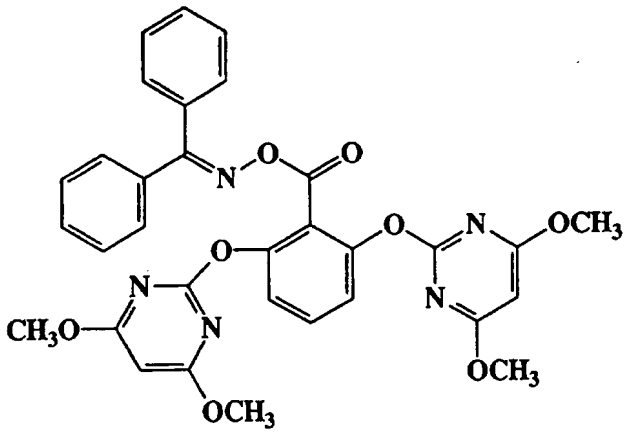
This invention relates to the safening of pyribenzoxim, with antidotal or safener compounds.

It is known that many herbicides injure crop plants at herbicide application rates needed to control weed growth. This renders many herbicides unsuitable for controlling weeds in the presence of certain crops. Where weed growth in crops is uncontrolled however, this results in lower crop yield and reduced crop quality, as weeds will compete with crops for nutrients, light and water. Reduction in herbicidal injury to crops without an unacceptable reduction in the herbicidal action can be accomplished by use of crop protectants known as " antidotes ", also sometimes referred to as " safeners " or "antagonists".

Pyribenzoxim, which is benzophenone O-{2,6-bis[(4,6-dimethoxypyrimidyl)oxy]benzoyl}oxime is known as a herbicide, see for example European Patent No. 658549. However, under certain conditions this can produce damage in crop plants, particularly cereal crop plants such as barley and wheat, and it is therefore the present invention seeks to provide a method for reducing the damage caused to crop plants by this compound.

Accordingly, the present invention provides a composition comprising:

(a) a herbicidally effective amount of pyribenzoxim, which is benzophenone O-{2,6-bis[(4,6-dimethoxypyrimidyl)oxy]benzoyl}oxime and has the formula (I):



(I)

and

(b) an antidotally effective amount of an antidote effective for (a);

in association with an agriculturally acceptable diluent or carrier.

The amount of antidote used in the compositions of the invention varies according to a number of parameters including the particular antidote employed, the crop to be protected, the amount and rate of herbicide applied, and the edaphic and climatic conditions prevailing. Also, the selection of the specific antidotes for use in the method of the invention, the manner in which it is to be applied and the determination of the activity which is non-phytotoxic but antidotally effective, can be readily performed in accordance with common practice in the art.

By "non-phytotoxic" is meant an amount of the antidote which causes at most minor or no injury to the desired crop species. By "antidotally effective" is meant an antidote used in an amount which is effective as an antidote to decrease the extent of injury caused by the herbicide to the desired crop species.

Preferably the weight ratio of herbicide (a) to antidote (b)is from about 10:1 to about 0.25:1, preferably from about 7:1 to about 0.5:1, more preferably from 4:1 to about 1:1, most preferably about 2:1.

Examples of the antidotes suitable for use in the present invention include the following:

(i) a compound of the formula (II):

$$R^{70}\text{-CO-NR}^{72}R^{71}$$

(II)

wherein R^{70} can be selected from the group consisting of haloalkyl; haloalkenyl; alkyl; alkenyl; cycloalkyl; cycloalkylalkyl; halogen; hydrogen; carboalkoxy; N-N-alkynylcarbamylalkyl; N-alkenylcarbamylalkoxyalkyl; N-alkyl-N-alkynylcarbamylalkoxyalkyl; alkynyloxy; haloalkoxy; thiocyanatoalkyl; alkenylaminoalkyl; alkylcarboalkyl; cyanoalkyl; cyanatoalkyl; alkenylaminosulfonalkyl; alkylthioalkyl; haloalkylcarbonyloxyalkyl; alkoxycarboalkyl; haloalkenylcarbonyloxyalkyl; hydroxyhaloalkyloxyalkyl; hydroxyalkylcarboalkyloxyalkyl; hydroxyalkyl; alkoxysulfonoalkyl; furyl; thienyl; alkyldithiolenyl; thienalkyl; phenyl; substituted phenyl wherein the substituents can be selected from halogen. alkyl, haloalkyl, alkoxy, carbamyl, nitro, carboxy and salts thereof, and haloalkylcarbamyl; phenylalkyl; phenylhaloalkyl; phenylalkenyl; substituted phenylalkenyl wherein the substituents can be selected from halogen, alkyl, alkoxy, and halophenoxy, phenylalkoxy; phenylalkylcarboxyalkyl; phenylcycloalkyl; halophenylalkenoxy; halothiophenylalkyl; halophenoxyalkyl; bicycloalkyl; alkenylcarbamylpyridinyl; alkynylcarbamylpyridinyl; dialkenylcarbamylbicycloalkenyl and alkynylcarbamylbicycloalkenyl;

R^{71} and R^{72}, which may be the same or different, are selected from the group consisting of alkenyl; haloalkenyl; hydrogen; alkyl;

haloalkyl; alkynyl; cyanoalkyl; hydroxyalkyl; hydroxyhaloalkyl; haloalkylcarboxyalkyl; alkylcarboxyalkyl; alkoxycarboxyalkyl; thioalkylcarboxyalkyl; alkoxycarboalkyl; alkylcarbamyloxyalkyl; amino; formyl; haloalkyl-N-alkylamido; haloalkylamido; haloalkylamidoalkyl; haloalkyl-N-alkylamidoalkyl; haloalkylamidoalkenyl; alkylimino; cycloalkyl; alkylcycloalkyl; alkoxyalkyl; alkylsulfonyloxyalkyl; mercaptoalkyl; alkylaminoalkyl; alkoxycarboalkenyl; haloalkylcarbonyl; alkylcarbonyl; alkenylcarbamyloxyalkyl; cycloalkylcarbamyloxyalkyl; alkoxycarbonyl; haloalkoxycarbonyl; halophenylcarbamyloxyalkyl; cycloalkenyl; phenyl; substituted phenyl wherein said substituents can be selected from alkyl, halogen, haloalkyl, alkoxy, haloalkylamido, phthalimido, hydroxy, alkylcarbamyloxy, alkenylcarbamyloxy, alkylamido, haloalkylamido and alkylcarboalkenyl; phenylsulfonyl; substituted phenylalkyl wherein said substituents can be selected from halogen or alkyl; dioxyalkylene; halophenoxyalkylamido-alkyl; alkylthiodiazolyl; piperidyl; piperidylalkyl; dioxolanylalkyl; thiazolyl; alkylthiazolyl; benzothiazolyl; halobenzothiazolyl; furyl; alkyl-substituted furyl; furylalkyl; pyridyl; alkylpyridyl; alkoxyazolyl; tetrahydrofurylalkyl; 3-cyano-thienyl; alkyl substituted thienyl; 4,5-polyalkylene thienyl; α-haloalkylacetamidophenylalkyl; α-haloalkylacetamidonitrophenylalkyl; α-haloalkylacetamidohalophenylalkyl; and cyanoalkenyl; or

R^{71} and R^{72} when taken together can form a structure consisting of piperidinyl; alkylpiperidinyl; pyridyl; di- or tetrahydropyridinyl; alkyltetrahydropyridyl; morpholyl; azabicyclononyl; diazacycloalkanyl; benzoalkylpyrrolidinyl; oxazolidinyl; perhydrooxazolidinyl; alkyloxazolidinyl; furyloxazolidinyl; thienyloxazolidinyl; pyridyloxazolidinyl; pyrimidinyloxazolidinyl; benzooxazolidinyl; C_{3-7}

spirocycloalkyl-oxazolidinyl: alkylaminoalkenyl; alkylideneimino; pyrrolidinyl; piperidonyl; perhydroazepinyl; perhydroazocinyl; pyrazolyl; -tetrahydro- or perhydroquinolyl or isoquinolyl; indolyl or di- or perhydroindolyl; and which combined R^{71} and R^{72} members can be substituted with those independent R^{71} and R^{72} radicals enumerated above; or

(ii) one of the following compounds:

α-[(cyanomethoxy)imino]benzeneacetonitrile;

α-[(1,3-dioxolan-2-ylmethoxy)imino]-benzeneacetonitrile;

O-[3-dioxolan-2-ylmethyl]-2,2,2-trifluoromethyl-4'-chloroacetophenone oxime;

benzenemethamine, N-[4-(dichloromethylene)-1,3-diotholan-2-ylidene]-α-methyl, hydrochloride;

diphenylmethoxy acetic acid methyl ester;

1,8-naphthalic anhydride;

4,6-dichloro-2-phenylpyrimidine;

2-chloro-N-[1-(2, 4, 6-trimethylphenyl)ethenyl]acetamide;

ethylene glycol acetal of 1,1-dichloroacetone;

benoxachor; dichlormid; fenclorim; or furilazole;

cloquintocet (5-chloroquinoline-8-yloxy acid) or a salt or ester thereof such as cloquintocet-mexyl (1-methylhexyl (5-chloroquinoline-8-yloxy) acetate);

fenchlorazole (1-(2,4-dichlorophenyl)-5-trichloromethyl)-1*H*-1,2,4-triazole-3-carboxylic acid), or a salt or ester thereof such as fenchlorazole-ethyl (ethyl 1-(2,4-dichlorophenyl)-5-trichloromethyl)-1*H*-1,2,4-triazole-3-carboxylate);

and mefenpyr-ethyl (diethyl 1-(2,4-dichlorophenyl)-5-methyl-2-pyrazoline-3,5-dicarboxylate).

Especially preferred antidotes for use in the present invention include: 2,2,5-trimethyl-N-dichloroacetyl oxazolidine; 2,2-dimethyl-5-phenyl-N-dichloroacetyl oxazolidine; 2.2-dimethyl-5-(2-furanyl)-N-dichloroacetyl oxazolidine; 2.2-dimethvl-5-(2-thienyl)- N-dichloroacetyl oxazolidine; N-N-diallyl dichloroacetamide; 2,2-spirocyclohexy-N-dichloroacetyl oxazolidine; 2,2-dimethyl-N-dichloroacetyl oxazolidine: 4-(dichloroacetyl)-3,4-dihydro-3-methyl-2H-1,4-benzoxazine; 3-[3-(dichloroacetyl)-2,2-dimethyl-5-oxalidinyl]pyridine;

4-(dichloroacetyl)-l-oxa -4-azapiro-(4,5)-decane; 2.2-dichloro-1-(1, 2,3, 4-tetrahydro -1-methyl-2-isoquinolyl)ethanone: cis/trans-1,4-bis(dichloroacetyl)-2,5-dimethylpiperazine: N- (dichloroacetyl)-1, 2, 3, 4-tetrahydroquinaldine: 1,5-bis(dichloroacetyl)-1,5-diaza cyclononane : 1-(dichloroacetyl)-1-azaspiro[4,4]nonane : α [(cyanomethoxy) imino] benzeneacetonitrile ; α-[(1,3-dioxolan-2-ylmethoxy)imino]benzeneacetonitrile: O-[1,3-dioxolan-2-ylmethyl] -2, 2, 2-trifluoromethyl-4'-chloroacetophenone oxime ; benzenemethamine; N-[4-(dichloromethylene) -1,3-dithiolan-2-ylidene]-α-methyl hydrochloride; diphenylmethoxy acetic acid, methyl ester; 1,8-naphthalic anhydride ;4,6-dichloro-2-phenylpyrimidine; 2-chloro-N-[1-(2, 4, 6-trimethylphenyl)ethenyl]-acetamide; cloquintocet, cloquintocet-mexyl; fenchlorazole, fenchlorazole-ethyl, mefenpyr-ethyl, and ethylene glycol acetal of 1,1-dichloroacetone.

More preferably (b) is selected from cloquintocet, cloquintocet-mexyl; fenchlorazole, fenchlorazole-ethyl and mefenpyr-ethyl.

In one embodiment (b) is more preferably cloquintocet, which is 5-chloroquinoline-8-yloxy acid; or a salt or ester thereof. Most

preferably (b) is cloquintocet-mexyl, which is 1-methylhexyl (5-chloroquinoline-8-yloxy) acetate.

In a second embodiment (b) is more preferably fenchlorazole, which is 1-(2,4-dichlorophenyl)-5-trichloromethyl)-1*H*-1,2,4-triazole-3-carboxylic acid, or a salt or ester thereof. Most preferably (b) is fenchlorazole-ethyl, which is ethyl 1-(2,4-dichlorophenyl)-5-trichloromethyl)-1*H*-1,2,4-triazole-3-carboxylate.

The compositions of the invention may also include a further pesticidally active ingredient, including herbicides, fungicides, insecticides and plant growth regulators. Herbicides are particularly preferred partners for example, 'fop' herbicides such as fenoxaprop, fenoxaprop-P, clodinafop, clodinafop-propargyl, a urea herbicide such as isopropturon or chlortoluron; flurtamone or diflufenican.

In another aspect of the invention there is provided a method of reducing phytotoxicity to crop plants caused by pyribenzoxim which comprises applying to the locus of the crop plant, the crop or crop plant seed an antidotally effective amount of an antidote effective to said compound.

The crops that may be protected by the method of the invention include cereal crops corn, rice, wheat, soybean, sorghum and cotton. The method of the invention is preferably performed where the crop to be protected is a cereal crop, particularly a spring cereal or winter cereal, such as barley, wheat and triticale, especially barley and wheat.

Weeds controlled by the combination include *Alopecurus myosuroides*, *Stellaria media*, *Veronica persica*, *Veronica hederifolia*, *Viola arvensis*, *Galium aparine*, and *Matricaria spp.*

The amount of pyribenzoxim applied depends on many factors, including but not limited to the weed species to be controlled, the crop

present, the timing of the application, the climatic conditions and the soil type. In general an application rate of pyribenzoxim of from about 70 to about 140g/ha is used.

The method of the invention is preferably applied post-emergence of the crop plant. In winter cereals the combination is preferably applied at the end of winter or in spring during the active growing period.

The following non-limiting example illustrates the invention.

Example 1

An experiment was carried-out to examine the damage barley following post-emergence applications of pyribenzoxim (hereafter "the Herbicide" and the safeners fenchlorazole-ethyl and cloquintocet-mexyl, alone and in tank mixtures. Control of *Alopecurus myosuroides* (ALOMY) was also investigated. All plant material was sown in 7cm pots filled with loam soil. The following species were tested:

Code	Species	Size at Application
HORVS	Barley var. Blenheim	3 - 4 leaves
ALOMY	*Alopecurus myosuroides*	3 leaves

The Herbicide, fenchlorazole-ethyl and cloquintocet-mexyl were applied as technical materials prepared in acetone. Mixtures of the Herbicide and safeners were applied at a ratio of 4:1, 2:1 and 1:1. Spray solutions were applied post-emergence using a laboratory sprayer to give a volume rate of 290 litres/ha. Each treatment was replicated 4 times and these were laid out in a glasshouse in a randomised block design. Plants were maintained in the glasshouse under good growing conditions with supplementary lighting and automatic irrigation. Plants were soil

watered on the day of application and 3 days after treatment and mat watered at all other times. Visual assessments were made 17 and 21 days after treatment (DAT). Damage was evaluated as percentage reduction in green area compared to control plants, where 0% represents no effect and 100% represents complete kill. In the Table that follows "Herbicide" refers to pyribenzoxim.

RESULTS

The treatment list and summary of the mean data are presented in Table 1 below.

Table 1: Mean percentage damage following post-emergence application of Pyribenzoxim alone and in tank mixtures with fenchlorazole-ethyl and cloquintocet-mexyl

		Barley	
Compound	**Rate (g/ha)**	**17 DAT**	**21 DAT**
Herbicide	16	13	26
Herbicide	32	10	15
Herbicide	64	26	54
Herbicide + fenchlorazole-ethyl	16 + 4	26	43
Herbicide + fenchlorazole-ethyl	32 + 8	13	23
Herbicide + fenchlorazole-ethyl	64 + 16	13	23
Herbicide + cloquintocet-mexyl	16 + 4	19	34
Herbicide + cloquintocet-mexyl	32 + 8	15	19
Herbicide + cloquintocet-mexyl	64 + 16	13	20
Herbicide + fenchlorazole-ethyl	16 + 8	35	53
Herbicide + fenchlorazole-ethyl	32 + 16	10	13
Herbicide + fenchlorazole-ethyl	64 + 32	6	20
Herbicide + cloquintocet-mexyl	16 + 8	3	3
Herbicide + cloquintocet-mexyl	32 + 16	4	6
Herbicide + cloquintocet-mexyl	64 + 32	3	5
Herbicide + fenchlorazole-ethyl	16 + 16	8	10
Herbicide + fenchlorazole-ethyl	32 + 32	14	13
Herbicide + fenchlorazole-ethyl	64 + 64	13	14
Herbicide + cloquintocet-mexyl	16 + 16	13	21
Herbicide + cloquintocet-mexyl	32 + 32	3	4
Herbicide + cloquintocet-mexyl	64 + 64	10	14
fenchlorazole-ethyl	32	10	14
fenchlorazole-ethyl	64	4	6
fenchlorazole-ethyl	125	1	3
cloquintocet-mexyl	32	3	5
cloquintocet-mexyl	64	8	18
cloquintocet-mexyl	125	4	6

Based on the criteria of a 50% or greater reduction in crop phytotoxicity, both fenchlorazole-ethyl and cloquintocet-mexyl safened pyribenzoxim at the highest application rate (64g/ha) in barley. Tests were also conducted in which the crop species was wheat (variety Minx) but there was insufficient phytotoxicity to determine whether the safeners provided an antidotal effect.

CLAIMS

1. A composition comprising:

(a) a herbicidally effective amount of pyribenzoxim, which is which is benzophenone O-{2,6-bis[(4,6-dimethoxypyrimidyl)oxy]benzoyl}oxime; and

(b) an antidotally effective amount of an antidote effective for (a);

in association with an agriculturally acceptable diluent or carrier.

2. A composition according to claim 2 in which (b) is 5-chloroquinoline-8-yloxy acid; or a salt or ester thereof.

3. A composition according to claim 2 in which (b) is cloquintocet-mexyl, which is 1-methylhexyl (5-chloroquinoline-8-yloxy) acetate.

4. A composition according to claim 5 in which (b) is 1-(2,4-dichlorophenyl)-5-trichloromethyl)-1*H*-1,2,4-triazole-3-carboxylic acid, or a salt or ester thereof.

5. A composition according to claim 4 in which (b) is fenchlorazole-ethyl, which is ethyl 1-(2,4-dichlorophenyl)-5-trichloromethyl)-1*H*-1,2,4-triazole-3-carboxylate.

6. A method of reducing phytotoxicity to crop plants caused by pyribenzoxim, which is benzophenone O-{2,6-bis[(4,6-dimethoxypyrimidyl)oxy]benzoyl}oxime, which comprises applying to

the locus of the crop plant, the crop or crop plant seed an antidotally effective amount of an antidote effective to pyribenzoxim.

7. A method according to claim 6 in which the antidote is 5-chloroquinoline-8-yloxy acid; or a salt or ester thereof.

8. A method according to claim 7 in which the antidote is cloquintocet-mexyl, which is 1-methylhexyl (5-chloroquinoline-8-yloxy) acetate.

9. A method according to claim 6 in which the antidote is 1-(2,4-dichlorophenyl)-5-trichloromethyl)-1*H*-1,2,4-triazole-3-carboxylic acid, or a salt or ester thereof.

10. A method according to claim 9 in which (b) is fenchlorazole-ethyl, which is ethyl 1-(2,4-dichlorophenyl)-5-trichloromethyl)-1*H*-1,2,4-triazole-3-carboxylate.

11. A method according to any one of claims 6 to 10 in which the crop is a cereal crop.

12. A method according to claim 11 in which the cereal crop is selected from wheat and barley.

13. A method according to any one of claims 6 to 12 by post-emergence application.

14. A composition according to claim 1 substantially as hereinbefore described.

15. A method according to claim 6 substantially as hereinbefore described.

The Patent Office

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Application No: GB 9804697.2
Claims searched: 1-15

Examiner: Stephen Quick
Date of search: 28 May 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): A5E (EE)

Int Cl (Ed.6): A01N

Other: Online: CAS ONLINE, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
Y	EP 0547546 A1	(HOECHST), see for example pages 6 (lines 21-26), 9 (lines 43-48, B1-6 in lines 30-31 & B2-1 in lines 28-29) & 13 (table, reference to B2-1)	1-15
Y	EP 0191736 A2	(CIBA-GEIGY), see especially pages 2 (line 4ff) & 9 (line 10)	1-15
Y	EP 0159290 A1	(CIBA-GEIGY), see especially pages 2 (line 5ff), 29 (Nr 107) & 48 (Nr 315)	1-15
Y	EP 0159287 A1	(CIBA-GEIGY), see especially pages 2 (line 16ff), 29 (Nr 107) & 49 (Nr 316)	1-15
Y	US 5698539 A	(HOECHST), see for example columns 1 (line 47ff), 7 (lines 16-27), 11 (lines 5-11) & 15 (lines 1-15)	1-15
Y	US 5296449 A	(CIBA-GEIGY), see especially columns 2 (lines 33-65) & 3 (lines 8-55)	1-15
Y	WO 97/45016 A1	(HOECHST SCHERING AGREVO), see especially pages 2 (1st complete paragraph) & 16 (last complete paragraph)	1-15

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
& Member of the same patent family
A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
E Patent document published on or after, but with priority date earlier than, the filing date of this application.

The Patent Office

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Application No: GB 9804697.2 **Examiner:** Stephen Quick
Claims searched: 1-15 **Date of search:** 28 May 1998

Category	Identity of document and relevant passage	Relevant to claims
Y	Chemical Abstracts, abstr no 128:98850 & Brighton Crop Prot. Conf.--Weeds, 1997, Vol. 1, pages 39-44, see abstract (LGC-40863 [Pyribenzoxim] as an acetolactate synthase (ALS) inhibitor)	1-15

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.